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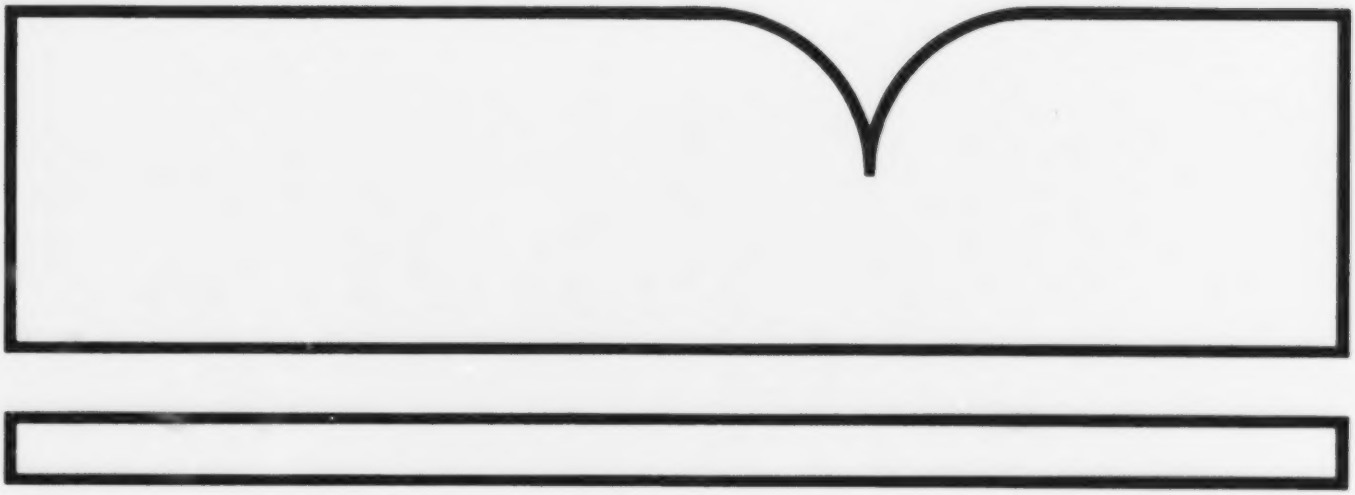

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JOURNAL ARTICLE

DETERMINING DISSOLVED HEXAVALENT CHROMIUM IN WATER AND WASTEWATER BY ELECTROTHERMAL ATOMIZATION*

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ABSTRACT

A procedure is described for separating dissolved hexavalent chromium (Cr^{6+}) from trivalent chromium (Cr^{3+}) and the water sample matrix by coprecipitation of lead chromate with lead sulfate in acetic acid solution. The supernatant is drawn off, and the Cr^{6+} precipitate is resolubilized with nitric acid, reduced to Cr^{3+}, and quantified by graphite furnace atomic absorption analysis. Included is a brief discussion on the chemistry of chromium and the approach used in the development of the method. Statements on the scope and application of the method, possible interferences, and a quality control step for verifying results are given. Precision and accuracy data are presented for tap water and various wastewater effluents. The method detection limit (MDL) for drinking water matrix is calculated to be 2.3 μg/L dissolved Cr^{6+}.

RESUME

Cette méthode décrit une procédure pour la séparation de chrome hexavalent dissous et de chrome trivalent dans un échantillon d'eau par coprécipitation de chromate de plomb avec du sulfate de plomb dans une solution d'acide acétique. Le surnageant est éliminé et le précipité de Cr^{6+} en solution avec de l'acide nitrique, réduit à Cr^{3+} et déterminé quantitativement par absorption atomique à four graphite. Cette publication comprend également une brève discussion sur la chimie du chrome et l'approche utilisée pour le développement de la méthode.
On donne également des informations quant aux possibilités d'application de la méthodes des interférences possibles et une procédure de contrôle de qualité pour la vérification des résultats. Nous présentons des données de précision et d'exactitude pour l'eau de ville et différents échantillons d'eau résiduaire. La détection limite de la méthode pour une matrice d'eau potable a été déterminée à 2,3 μg/L de Cr^{6+} dissous.

ZUSAMMENFASSUNG

Diese Methode beschreibt ein Verfahren zur Trennung von gelöstem, sechswertigen Chrom (Cr^{6+}) von dreiwertigen (Cr^{3+}) und der Wasserprobenmatrix durch Mitfällen von Bleichromat mit Bleisulfat in essigsaurer Lösung. Der Überstand wird abgesaugt und der Cr^{6+} Niederschlag mit Salpetersäure gelöst, zu Cr^{3+} reduziert und durch Graphitrohrofen-Atomabsorptions-Analyse quantitativ bestimmt. Es wird auch die Chemie des Chrom sowie das bei der Entwicklung der Methode verwendete Verfahren kurz diskutiert. Feststellungen über den Bereich und die Anwendung der Methode sowie über mögliche Interferenzen werden ebenso gegeben wie eine Kontrollmöglichkeit zur Überprüfung der Ergebnisse. Daten über Genauigkeit und Richtigkeit werden für Trinkwasser und verschiedene Abwässer angegeben. Die methodische Nachweisgrenze (MDL) für Trinkwasser berechnet sich zu 2,3 μg/L gelöstes Cr^{6+}.

INTRODUCTION

Chromium is an important element to man. It is considered an essential element in his diet with the average daily intake being below 100 μg. It has been reported that a chromium deficiency can impair glucose metabolism in older people, while excessive concentrations are toxic in enzyme and bacterial systems. Chromium can exist in two different but stable valence states – trivalent (Cr^{3+}) and hexavalent (Cr^{6+}). Hexavalent chromium is considered to be a more toxic form because of its oxidizing potential and easy permeation of biological membranes. It is believed that all biological interaction with Cr^{6+} will result in its reduction to the trivalent form, which complexes with protein and nucleic acids. Since Cr^{6+} is toxic to some aquatic life, its concentration in surface water is of definite concern. As for man, a significant part of his nondietary exposure to Cr^{6+} is from the environment. The following discussion and analytical method present one approach to monitoring dissolved Cr^{6+} in water and wastewater (1, 2).

*This report has been reviewed by the Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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DISCUSSION

Chemical Properties

In water and wastewater, chromium can be present in either valence state. Although the trivalent chromium is the more stable of the two forms, it can be oxidized to the hexavalent state with an acid permanganate or persulfate digestion. In alklaline solution, it has a much lower oxidation potential where it can be readily oxidized to the chromate ion with hydrogen peroxide or by aeration (3).

$$Cr(OH)_3 + 5OH^- = CrO_4^{2-} + 4H_2O + 3e^- \quad E^0 = 0.13\ V$$

The chromic ion (Cr^{+++})does not exist as a free ion in solution, but is hydrated or complexed with some other anion – nitrate, chloride, sulfate, etc. In acid solution, Cr^{3+} will form a stable complex with the anion of the acid. Trivalent chromium complexes are relatively kinetically inert and changes due to pH tend to occur very slowly. These complexes can therefore remain in solution for long periods of time. Near neutral pH and above, Cr^{3+} can precipitate as chromic hydroxide which can be dissolved in acid when freshly precipitated but becomes insoluble with aging or heat. Along with chromic oxide, most chromites are also insoluble in water and therefore if present in a water sample, would be in the suspended material.

The behavior of hexavalent chromium in water, how-

ever, is quite different from that of the trivalent form. Many chromates are soluble in water and above pH 6, Cr^{6+} is most likely to occur in solution as the chromate ion (CrO_4^{2-}). If the pH is lower, between 2 and 6, the dichromate ion ($Cr_2O_7^{2-}$) and $HCrO_4^-$ are in equilibrium.

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \quad K = 10^{-5.9}$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \quad K = 10^{-2.2}$$

Below pH 1, H_2CrO_4 is the main species. Although the chromate ion is relatively stable, the dichromate in acid solution is a strong oxidizer and in the presence of organic material or easily oxidized compounds, is readily reduced.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O \quad E^0 = 1.33V$$

The chromate ion will form insoluble chromates in the presence of lead, barium, mercury, silver, thallium, and bismuth (4, 5).

Analytical Procedures

A water sample containing suspended material may have both valence states of chromium present in each of the suspended and dissolved fractions of the sample. The desired method would be one where the concentrations of the two species in each fraction could be quantitatively determined. Unfortunately, at present, there is no tested method that will assure no valence state alteration from sample matrix interaction. Consequently, only total chromium (dissolved plus suspended) is measured without regard to the valence state. The analytical approach is either to solubilize the chromium in the suspended fraction by acid digestion followed by direct aspiration atomic absorption (6, 7) or to convert the total chromium to the hexavalent state with an acid permanganate digestion followed by analysis using a chelation/extraction atomic absorption method (8) or a diphenyl carbazide procedure (9–11). Where the measured value for total chromium in a sample is below the drinking water regulatory limit of 0.05 mg/L, there has been little concern over the Cr^{6+} concentration.

Recent investigations have centered on method development work for dissolved Cr^{6+}. Except for the insoluble chromates, which are believed to be inert to change in the aquatic environment, it is assumed that all other forms of Cr^{6+} are soluble in water at or near neutral pH (12). Samples are filtered through a 0.45-μm filter to separate the dissolved constituents from the suspended material, but are not acidified upon collection in order to prevent accelerated reduction of Cr^{6+}. The two valence states in the filtrate are then separated, and the hexavalent form is analyzed by either atomic absorption analysis or a colorimetric diphenyl carbazide method. If ion exchange columns are used for separation, the pH of the solution placed on the column is critical since it can affect the chromium adsorption on the resin, band separation, and oxidation of the resin by the chromate ion. Low recoveries have been attributed to the length of elution time and possible channeling of the resin (13). With the chelation/extraction technique of separation, the efficiency of the extraction is also affected by pH as well as shaking rate and time. Reduction of Cr^{6+} is of prime concern with the pyrrolidine dithiocarbamic acid procedure because the solution must be adjusted to pH 2 for complete extraction (14). This is also true for the diphenyl carbazide method where a low pH is required for full color development. Not all sample matrices are compatible with chelation/extraction inasmuch as an emulsion or heterogeneous mixture is formed at the liquid interface with some wastewaters thus preventing quantitative separation. In addition, the chelate used in the chelation/extraction procedures referenced are not specific to chromium but are used mainly for multielement extraction. A high concentration of another extractable element could be competitive and cause incomplete extraction of the chromium.

Method Description

Because of problems encountered in the analysis of some wastewater samples when using chelation/extraction methodology, the technique of coprecipitation was investigated. Some workers have concentrated and separated chromium from seawater by coprecipitation with ferric hydroxide $Fe(OH)_3$ (15). But only partial separation was reported for Cr^{6+} unless it was first reduced to the trivalent form, after which nearly complete precipitation was achieved. Since this coprecipitation was completed above the neutral pH where Cr^{6+} is soluble, it is believed the partial precipitation of Cr^{6+} was attributed to occlusion or adsorption of the chromate ion on the $Fe(OH)_3$. For this reason and the concern that Cr^{3+} may be oxidized to Cr^{6+} in an alkaline medium, the approach of determining the Cr^{6+} remaining in solution after the precipitation of Cr^{3+} was not considered.

A second approach, considered but not pursued, was to analyze the sample solution before and after the precipitation of Cr^{6+} and determine the Cr^{6+} by difference. The concerns with this approach were threefold. First, the analysis would require two measurements which would increase the variance, thereby making the determination less precise. Second, the analysis would be done in the original sample matrix increasing the possibility of the need for the method of standard additions. Third, it was learned during the course of this work that there is a distinct difference in the atomic absorption responses of Cr^{6+} and Cr^{3+} in furnace analysis. Furthermore, when using pyrolytic graphite*, the absorption signal of Cr^{6+} in a water sample matrix is not linear, but experiences an upward curvature that increases with increasing concentration. Just the opposite is true for both Cr^{6+} and Cr^{3+} in nonpyrolytic graphite. There, 10 mg/L of calcium (Ca) gives a suppression of 10%, which increases with increasing Ca concentration to constant suppression of approximately 20% between 50 mg/L and 100 mg/L Ca. Overall, the use of nonpyrolytic graphite is preferred when determining chromium because it results in better reproducibility and a greater analytical working range. The coprecipitation method described in this article avoids the potential problem and concern listed above and is one where the determination of Cr^{6+} is by direct measurement. The method has been prepared in a format for inclusion in *Methods for Chemical Analysis of Water and Wastes* EPA-600/4-79-020 and will be titled "Chromium, Dissolved Hexa-

*Although not confirmed in this work but according to the manufacturer, the problems experienced with the pyrolyte graphite tubes were attributed to an earlier coating process no longer used on the tubes that are presently available.

valent Method 218.5 (Atomic Absorption, furnace technique)." In addition to the summary given in Section 2 of the method write-up, the following comments should assist the analyst in understanding the various steps of the procedure.

1. After filtration, a measured aliquot of filtrate is adjusted with dilute acetic acid to pH 3.5 ± 0.3. The aliquot for analysis needs to be adjusted to a pH < 5 to prevent precipitation of lead hydroxide upon the addition of lead nitrate (16). A pH of 3.5 was selected because of experimentally determined good recoveries (> 85%) of Cr^{6+} concentrations normal to furnace analysis. The use of a pH meter is preferred for this operation. The volume change due to the addition of dilute acetic acid should be noted and, if greater than 2%, should be used to correct the final result. Acetic acid is used because of the low solubility of lead chromate in acetic acid. Other acids, such as hydrochloric and sulfuric, should be avoided since they react and form the chlorochromate ion or sulfate complex.
2. After addition of the lead nitrate solutions resulting in the formation of lead chromate, glacial acetic acid is added to ensure that Cr^{3+} and other elements remain in solution. Addition of ammonium sulfate provides adequate sulfate for complete precipitation. Once the supernatant has been drawn off, the Cr^{6+} precipitate is solubilized with nitric acid and reduced to Cr^{3+} with hydrogen peroxide. Calcium nitrate is added to provide for a uniform matrix, and the sample is analyzed in an argon atmosphere using nonpyrolytic graphite and simultaneous background correction.
3. The approach used in this method has some distinct advantages.
   a. Loss or contamination due to solution transfer is not a problem. After pH adjustment, the remaining part of the analysis is carried out in the same 15-mL stoppered centrifuge tube.
   b. The method requires readily available equipment and reagents generally found in a normal laboratory operation.
   c. The analysis solution to be injected into the furnace has been separated from the original sample matrix thereby reducing the need for the method of standard additions.
   d. All atomic absorption measurements are made with chromium in the same valence state and in a uniform matrix.
   e. A quality control step for verifying the result or to detect the possible reduction of Cr^{6+} by the sample matrix is given as a part of the method. It should be noted that it is also possible to determine the total (Cr^{6+} + Cr^{3+}) dissolved chromium by analyzing a second aliquot of the filtrate after adding the appropriate amounts of nitric acid, hydrogen peroxide, and calcium nitrate. The result, however, must be corrected for the volume change and a spike analyzed to determine if the method of additions is required.
4. There are also some disadvantages with the method.
   a. Lowering the pH after filtration can result in reduction of Cr^{6+}, especially if the pH is inadvertently taken to a pH of 2 or lower. If reduction is due to the presence of sulfide or sulfite, the sample should be neutralized and aerated before pH adjustment. The usefulness of this suggestion depends on the nature of the sample matrix and must be verified using the recommended quality control step given in Section 10.1.
   b. If chloride and/or sulfate are in excess of 1000 mg/L, interferences occur mainly in the precipitation step. Dilution of the sample before analysis is required to correct this situation.

*STORET (STOrage and RETrieval) is EPA's computerized information system that draws on data from two hundred remote locations in an attempt to define the causes and effects of water pollution. Hexavalent chromium data are entered into the system using the listed parameter code number.

METHOD

CHROMIUM, DISSOLVED HEXAVALENT METHOD 218.5 (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

STORET No. 01032*

1. Scope and Application
   1.1 This method covers the determination of dissolved hexavalent chromium (Cr^{6+}) in drinking and surface waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that potential interfering substances are taken into account. (See 4.1.)
   1.2 The method may be used to analyze samples containing from 5 to 100 μg of Cr^{6+} per liter. The range of the method may be extended upward by dilution.
2. Summary of Method
   2.1 The method is based on the separation of Cr^{6+} from the sample by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernatant is drawn off and the Cr^{6+} precipitate resolubilized in nitric acid as trivalent chromium (Cr^{3+}) and quantified by furnace atomic absorption.
3. Sample Handling and Preservation
   3.1 For sample handling, cleaning glassware, and the filtration procedure see part 4.1 of the Atomic Absorption Method section of reference 14.
   3.2 The sample must not be preserved by acidification, but instead must be transported and stored at 4°C until the time of analysis.
   3.3 Stability of Cr^{6+} in environmental samples is not completely understood at this time. The chemical nature of the sample matrix can have a definite effect on the chemistry of chromium. Therefore, the analysis should be carried out as soon as possible but no longer than 24 hours after collection.
4. Interferences
   4.1 The possible interference from other elements

which form stable chromates is not known at this time.

4.2 Samples with either sulfate or chloride concentrations above 1000 mg/L should be diluted before analysis.

4.3 The potential reduction of Cr^{6+} from highly reductive substances increases as pH is lowered. When sulfites and sulfides are present, the sample aliquot taken for analysis should be neutralized and aerated before beginning.

5. Instrument Parameters (General)

5.1 Drying time and temp: 30 sec at 125°C

5.2 Ashing time and temp: 30 sec at 1000°C

5.3 Atomizing time and temp: 10 sec at 2700°C

5.4 Purge gas atmosphere: argon

5.5 Wavelength: 357.9 nm

5.6 Other operating parameters should be as specified by the particular instrument manufacturer.

6. Special Apparatus

6.1 Glassware

6.1.1 Filtering flask, heavy wall, 1-liter capacity

6.1.2 Centrifuge tubes, heavy duty, conical, graduated, glass-stoppered, 10-mL capacity

6.1.3 Pasteur pipets, borosilicate glass, 5¾ inches

6.2 Centrifuge: Any centrifuge capable of reaching 2000 rpm and accepting the centrifuge tubes described in 6.1.2 may be used.

6.3 pH meter: A wide variety of instruments is commercially available and suitable for this work.

6.4 Test tube mixer: Any mixer capable of thorough vortexing is acceptable.

7. Reagents

7.1 Lead nitrate solution: Dissolve 33.1 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.2 Ammonium sulfate solution: Dissolve 2.7 g of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.3 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL (1 mL = 20 mg Ca).

7.4 Nitric acid, conc: distilled reagent grade or equivalent to spectrograde quality

7.5 Acetic acid, glacial: ACS reagent grade

7.5.1 Acetic acid, 10% (v/v): Dilute 10 mL glacial acetic acid to 100 mL with deionized distilled water.

7.6 Ammonium hydroxide, 10% (v/v): Dilute 10 mL conc ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with deionized distilled water.

7.7 Hydrogen peroxide, 30%: ACS reagent grade

7.8 Potassium dichromate standard solution: Dissolve 2.8285 g of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in deionized distilled water and dilute to 1 L; 1 mL = 1 mg Cr (1000 mg/L).

7.9 Trivalent chromium working stock solution: To 50 mL of the potassium dichromate standard solution (7.8) add 1 mL of 30% H_2O_2 (7.7) and 1 mL conc HNO_3 (7.4) and dilute to 100 mL with deionized distilled water; 1 mL = 0.5 mg Cr^{3+}. Prepare fresh monthly or as needed.

8. Calibration

8.1 At the time of analysis prepare a blank and a series of at least four calibration standards from the Cr^{3+} working stock (7.9) that will adequately bracket the samples. The normal working range covers a concentration range of 5 to 100 μg Cr/L. Add to the blank and each standard 1 mL 30% H_2O_2 (7.7), 5 mL conc HNO_3 (7.4), and 1 mL calcium nitrate solution (7.3) for each 100 mL of prepared solution before diluting to final volume. These calibration standards should be prepared fresh weekly or as needed.

8.2 The listed instrumental conditions (5.) and the stated calibration concentration range are for a Perkin-Elmer HGA-2100 based on the use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite tubes. The use of simultaneous background correction is required for both calibration and sample analysis.

9. Procedure

9.1 Transfer a 50-mL portion of the filtered sample to a 100-mL Griffin beaker and adjust to pH 3.5±0.3 by adding 10% acetic acid dropwise. Record the volume of acid added and adjust the final result to account for the dilution.

NOTE: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to <3, 10% NH_4OH (7.6) should be used to raise the pH to above 3.

9.2 Pipet a 10-mL aliquot of the adjusted sample into a centrifuge tube (6.1.2). Add 100 μL of the lead nitrate solution (7.1), stopper the tube, mix the sample, and allow to stand for 3 minutes.

9.3 After the formation of lead chromate, retain the Cr^{3+} complex in solution by addition of 0.5 mL glacial acetic acid (7.5). Stopper and mix.

9.4 To provide adequate lead sulfate for coprecipitation add 100 μL ammonium sulfate solution (7.2), stopper, and mix.

9.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2000 rpm in small increments over a period of 5 minutes. Centrifuge the sample at 2000 rpm for 10 minutes.

NOTE: The speed of the centrifuge must be increased slowly to insure complete coprecipitation.

9.6 After centrifuging, remove the tube and draw off the supernatant using the apparatus detailed in Figure 1. As the Pasteur pipet is lowered into the tube, the supernatant is sucked into the filtering flask. With care the supernatant can be withdrawn to within approximately 0.1 mL above the precipitate.

9.7 To the remaining precipitate add 0.5 mL conc HNO_3 (7.4), 100 µL 30% H_2O_2 (7.7), and 100 µL calcium nitrate solution (7.3). Stopper the tube and mix using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10 mL, mix, and analyze in the same manner as the calibration standard (8.2).

9.8 For the general furnace procedure and calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of reference 14.

10. Verification

10.1 For every sample matrix analyzed verification is necessary to determine that neither a reducing condition nor a chemical interference affecting precipitation is present. This must be accomplished by analyzing a second 10-mL aliquot of the pH adjusted filtrate (9.1) spiked with Cr^{6+} (7.8). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be of less than 30 µg Cr/L. To verify the absence of an interference the spike recovery should be between 85% and 115%.

10.2 If the addition of the spike extends the concentration beyond the range of the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

10.3 If the verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

11. Analytical Notes

11.1 Nitrogen should not be used as a purge gas because of possible CN band interference.

11.2 The use of pyrolytic graphite should be avoided when possible. Generally, pyrolytic graphite resulted in a more limited analytical working range and in some situations an enhancement effect.

11.3 Pipet tips have been reported to be a possible source of contamination. (See part 5.2.9 of the Atomic Absorption Methods section of reference 14.)

11.4 The method of standard additions should not be required inasmuch as the Cr^{6+} has been separated from the original sample solution and redissolved in a uniform matrix having an absorption response coincident to the calibration curve.

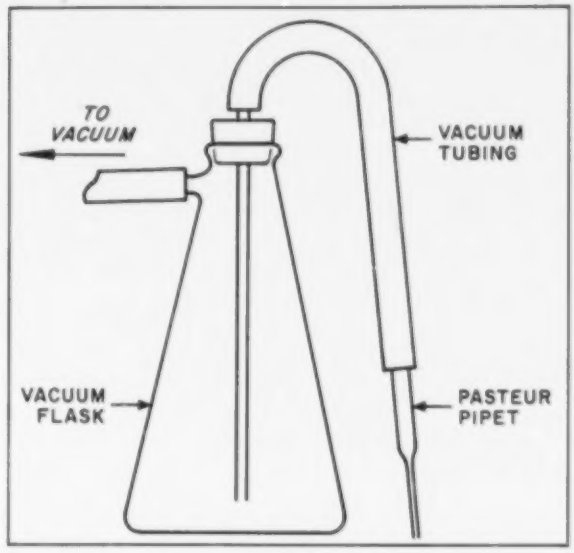

Fig. 1. Schematic of apparatus used to withdraw supernatant.

11.5 Data to be entered into STORET (No. 01032) must be reported as µg/L.

12. Precision and Accuracy. See Table I.

RESULTS

Listed in Table I are precision and accuracy data collected from the analyses of spiked drinking water and various wastewater matrices. The effluent samples were analyzed for both dissolved Cr^{6+} and dissolved total chromium (Cr^{6+} + Cr^{3+}) to determine that both species were present in solution. After analysis, aliquots of these samples were spiked with either Cr^{6+} or Cr^{3+} and reanalyzed to confirm the specificity and accuracy of the method. It should be noted that the tannery and plating waste effluents required dilution before analysis. The actual dissolved Cr^{6+} and dissolved total (Cr^{6+} + Cr^{3+}) in the tannery effluent were 180 and 280 µg/L, respectively, while the concentration of the plating waste was 240 and 250 µg/L, respectively.

To show the applicability of the method to the analysis of low concentrations in drinking water, Cincinnati, Ohio tap water was spiked at three concentration levels of Cr^{6+} and analyzed. The analytical results are included in Table I and indicate the acceptability of the method for this type of analysis. The data from the 5-µg/L determination were used to calculate the method detection limit (MDL) (17) at the 99% confidence level. The calculated MDL in Cincinnati, Ohio drinking water is 2.3 µg/L.

To demonstrate that a disproportionate or relatively high concentration of Cr^{3+} does not interfere with the method, three standard solutions of Cr^{3+} were carried through the method as samples. The results of these determinations are given in Table II and reveal that separation is nearly complete with a positive bias of approximately 1%.

SUMMARY

The coprecipitation method described in this article is a viable alternate procedure to chelation/extraction or

TABLE I
Precision and Accuracy Data
Single Laboratory – EMSL-Cincinnati

Sample type + spike	Dissolved Cr^{6+}: Number of replicate determinations	Dissolved Cr^{6+}: Average amount detected (µg/L)	Dissolved Cr^{6+}: % Spike recovery	Dissolved Cr^{6+}: % Relative standard deviation	Dissolved total (Cr^{6+} + Cr^{3+}): Average amount detected (µg/L)	Dissolved total (Cr^{6+} + Cr^{3+}): % Spike recovery	Dissolved total (Cr^{6+} + Cr^{3+}): % Relative standard deviation
Domestic – industrial sewage effluent	7	22		4.5	29		2.4
+ 50 µg/L Cr^{6+}	7	69	94	3.9	77	96	0.4
Tannery effluent	4	28		3.6	44		4.6
+ 38 µg/L Cr^{3+}	4	29		6.4	80	94	0.8
+ 40 µg/L Cr^{6+}	4	66	96	3.9	83	97	4.5
Plating waste effluent	4	48		1.7	51		2.1
+ 38 µg/L Cr^{3+}	2	51		1.2	85	89	0.5
+ 40 µg/L Cr^{6+}	2	85	93	0.6	94	108	0.3
Cincinnati tap water	2	ND			ND		
+5 µg/L Cr^{6+}	7	5.1	102	14.4			
+ 10 µg/L Cr^{6+}	7	10.2	102	6.2			
+ 50 µg/L Cr^{6+}	4	51	102	1.1			

ND = not determined, less than MDL.

TABLE II
Hexavalent Analysis of Trivalent Standard

Cr^{3+} concentration (µg/L)	Number of replicate determinations	Average amount Cr^{6+} detected (µg/L)	% Relative standard deviation
200	3	2.4	31
500	3	5.2	36
1000	3	7.9	19

colorimetric procedures for the determination of hexavalent chromium. Furnace analysis atomic absorption is employed for specificity and sensitivity. A quality control step for the verification of results has been included with the demonstrated precision and accuracy needed for water and wastewater analysis. The method can be conveniently used for the analysis of a variety of samples, but is probably most useful in the analysis of those samples where the matrix prevents clear separation between aqueous and organic solvent phases of a chelation/extraction procedure.

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